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Ordering and Steric-Hardening in SBS-Modified Bitumen

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Styrene−butadiene−styrene (SBS)-modified bitumen shows good cracking resistance at low temperatures. With the knowledge of the microstructure of SBS-modified bitumen being incomplete, the reasons for the low-temperature performance remain partly unclear. In this work, modulated differential scanning calorimetry (MDSC) was used to study the ordering of crystallizable alkanes and that of alkyl aromatics in SBS-modified bitumen. These compounds are responsible, respectively, for the cold-crystallization (CC) and the steric-hardening (SH) visible on the nonreversing heat-flow (NRHF) curves obtained from MDSC. In blends of bitumen with 3, 6, and 10 wt % SBS, CC and SH enthalpies were measured. SBS was found to reduce both the CC and the SH in bitumen, the reduction being disproportionately higher than expected on the basis of polymer concentration. The loss of CC and SH enthalpies demonstrate the reduced capacity of alkanes and alkyl aromatics to order in the presence of SBS.

Introduction

Bitumen is commonly modified with a styrene−butadiene−styrene (SBS) block copolymer.[1,2] The blend is used as a binder in asphalt concrete for roadways and in membranes for the waterproofing of roofs and buried Portland cement concrete foundations. By itself, bitumen shows viscoelastic properties very sensitive to temperature.[3,4] At low temperatures, it is brittle; at high temperatures, it deforms or flows easily. In contrast, SBS-modified bitumen shows improved resistance to cracking in winter[5] and resistance to flow in summer.[6]

The viscoelastic properties of such blends say little about the compatibility of the blend components and their interactions or about the phases in the modified binders. Very early, it was demonstrated that SBS is swollen with saturates and aromatics,[7] observations that imply an interaction of the copolymer with these bitumen fractions. More recently, we reported on the mixing of the amorphous phases in SBS−bitumen blends[8] by measuring shifts in glass transition temperatures (T_g). A mixed phase was found to exist in the blends, where the polybutadiene block is swollen with 30% of the maltenes. The results indicated that the PB block interacted strongly with bitumen, while the PS block interacted only weakly.

In this paper, we report on the effect of SBS on the ordering of alkanes and alkyl aromatics in its blends with bitumen. The alkanes are responsible for the cold-crystallization in bitumen, whereas the alkyl aromatics are responsible for the steric-hardening.[9] It was found that the addition of SBS to bitumen results in decreased enthalpies associated with the cold-crystallization of alkane segments and the steric-hardening associated with the partial ordering of asphaltenes.

Experimental Section

The materials and the MDSC method are those described in detail before.[10,11] The blends contained 3, 6, and 10 wt % linear SBS. After their preparation, all blends were annealed for 24 h at room temperature before being analyzed. For the MDSC, the samples were quench-cooled from room temperature to −120 °C in the calorimeter and then equilibrated for 5 min before being heated to 150 °C at 3 °C/min. Neat bitumen was analyzed before and after 24 h of annealing. The nonreversing heat flows reported are those obtained from the total heat flow after its deconvolution from the reversing heat flow.[10−13]

Results and Discussion

The total heat flow from standard DSC for blends of bitumen with 0−10% SBS is shown in Figure 1. As with other DSC results,[14] only the predominant bitumen glass transition temperature is visible, and any change in T_g with an increase in SBS content is difficult to discern. We reported earlier on the benefits of MDSC to study the variation in T_g in the blends.[8]

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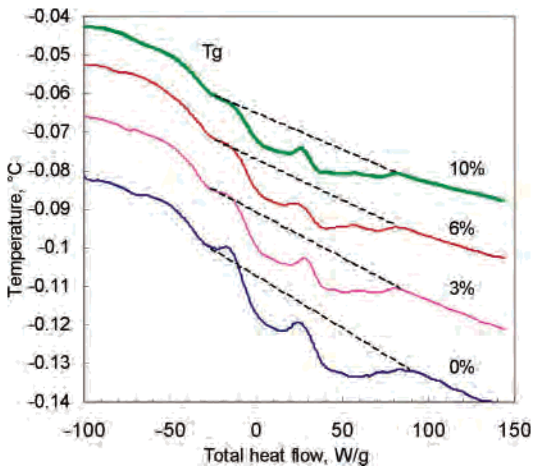

Figure 1. Typical DSC curves for blends of bitumen with 0−10 wt % SBS.

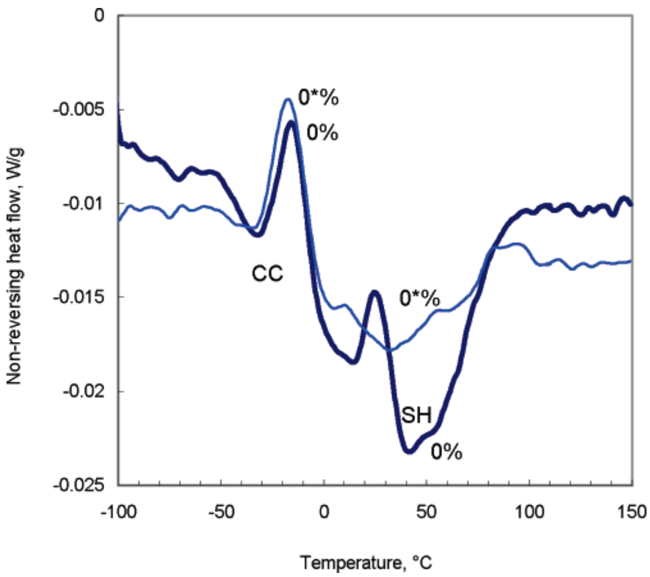

Figure 2. Nonreversing heat-flow curves obtained upon heating annealed (0%) and unannealed (0*%) bitumen. See text for details.

The curves in Figure 1 also show a broad endothermic envelope, as highlighted by the dashed lines. Bitumen shows a cold-crystallization exotherm at −20 °C, which seems to disappear in the blends. There is also a decrease in the size of the endothermic envelope between about −20 and 90 °C. Both the exotherm and the endotherm arise from ordered fractions in bitumen.[10,11] Given their overlap with multiple glass transitions in bitumen,[8,10] the DSC analysis of the change in enthalpies in blends with SBS can only remain qualitative.

The deconvolution of the DSC signal in Figure 1 by Fourier analysis of the temperature-modulated signal[12] allowed us to focus on the events that occur in the endothermic envelope. The nonreversing heat-flow (NRHF) curves from modulated DSC experiments on SBS−bitumen blends are shown in Figures 2 and 3. The annealed and unannealed neat bitumen are labeled 0% and 0*% SBS, respectively. Figure 2 shows that, by itself, the bitumen under investigation has a cold-crystallization (CC) exotherm at −12 °C followed by a split endotherm, the portion between 30 and 80 °C being time-dependent.[9] There is a small endotherm at 30−80 °C in freshly melted bitumen (0*% SBS in Figure 2), an area where saturates are known to melt. Overlapping with this endotherm is a second endotherm, which after 24 h of annealing at room temperature, has grown to >80% of its full size (0% SBS). It has been shown that this endotherm

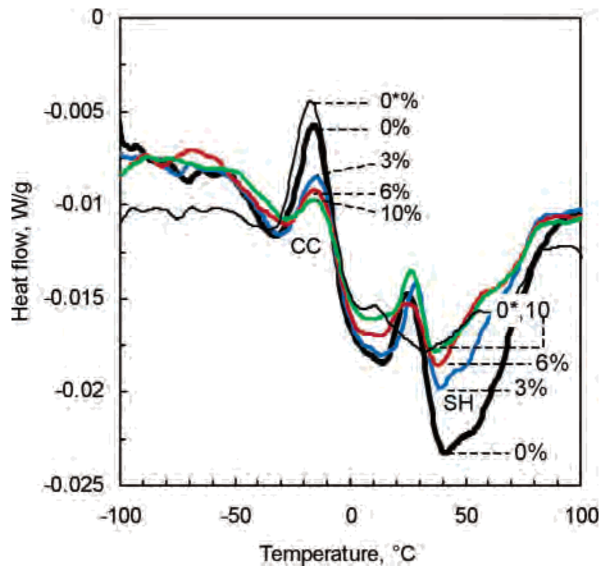

Figure 3. Nonreversing heat-flow curves for bitumen−SBS blends with 0−10% SBS. See text for details.

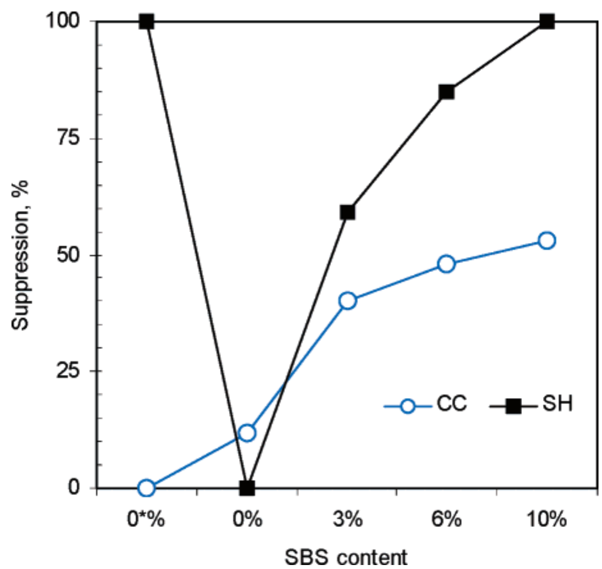

Figure 4. Suppression of steric-hardening (SH) and cold-crystallization (CC) due to SBS.

arises from asphaltenes,[9−11] which are thought to order into a liquid-crystalline-like mesophase.[10] The ordering of the asphaltenes governs the stiffening of bitumen at room temperature,[9] a process referred to as steric-hardening (SH). The cold-crystallization exotherm found at 25 °C arises from saturated alkane segments that crystallize upon heating,[9] the segments being found mostly in the bitumen saturates and aromatics fractions.[11]

In blends with bitumen, SBS affects both the CC and the SH (Figure 3). An increase in SBS content leads to an increased suppression of cold-crystallization (peak centered at −17 °C) and demonstrates that SBS affects crystallizable fractions. In other words, SBS mixes with saturates and aromatics, an observation which is consistent with previous studies.[7,8] The extent of the effect of SBS on CC, as shown in Figure 3, was not visible by DSC. The results in Figure 1 indicated that 3% SBS prevented all CC, an effect not substantiated by the MDSC results in Figure 3.

SBS also suppressed the ordering of the asphaltenes, as seen from the reduction in the endotherm symptomatic of steric-hardening, between 40 and 90 °C. This suggests that SBS also interacts with the asphaltenes. This is consistent with a shift in T_g of the asphaltenes in SBS-modified bitumen.[8]

Figure 4 shows a plot of the intensity of the CC exotherm and the SH endotherm. For convenience of interpretation, this intensity is shown as percent suppression. It shows that 3% SBS led to a 40% suppression in CC and to a 60% suppression in SH. The suppression rises with the polymer content, such that 10% SBS led to a 50% reduction in CC and a complete disappearance of SH. The disproportionately high suppression in CC and SH versus the SBS weight content suggests a volumetric rather than a weight effect.

The effect of SBS on CC and SH in bitumen is of practical importance as it may help explain the improved low-temperature properties and reduced cracking propensity[6] found when SBS is blended with bitumen. This improvement in performance is often attributed to the formation of a bitumen−SBS phase with a T_g lower than that for bitumen.[8] The results in Figures 3 and 4 demonstrate that another mechanism is also at play: the hindrance of bitumen ordering. In other words, SBS prevents the crystallization of the saturated segments in bitumen and the mesophasic ordering of its asphaltenes. These suppressions translate into a larger amorphous content. Amorphous materials have increased molecular mobility, larger free volumes, and more rapid relaxations than ordered phases.[15] On a macroscale, a benefit of increased free volume is a depression in cracking temperature.[16]

Conclusions

The ordering of bitumen phases in SBS-modified binders was investigated with MDSC. It was shown that SBS hinders the cold-crystallization of crystallizable bitumen segments and the ordering of the asphaltenic mesophase responsible for steric-hardening. This is a second mechanism by which the susceptibility to low-temperature cracking may be improved.

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